# Catalysis Tutorial

Part k_1

What does a catalyst (not) do?

- A catalyst is a substance that, when added to a reaction or process, provides a new pathway with a lower activation barrier.

- A catalyst *cannot* make a reaction more favorable (no effect on ΔG_{rxn}).

- A catalyst lowers the activation barrier of both forward and reverse reactions.

ΔG^*

$\Delta G_{RV}{}^*$

$\Delta G_{RVcat}{}^*$

$\Delta G_{cat}{}^*$

ΔG_{rxn}

Reactants

Products
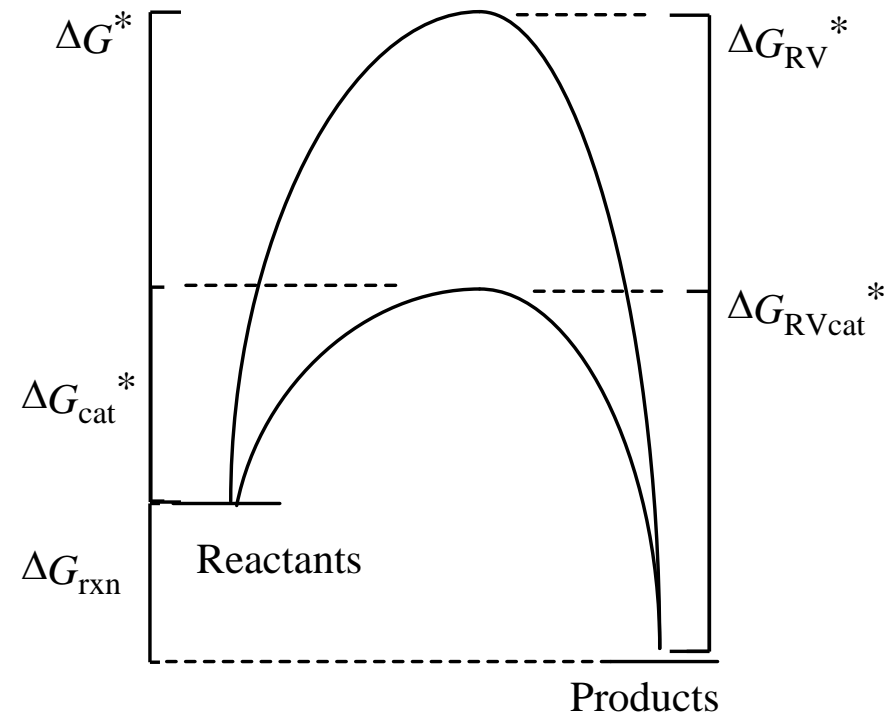
Equilibrium and Rate

- The thermodynamic favorability of a reaction (ΔG_{rxn}) can be expressed as the equilibrium constant.

$$a\, A + b\, B \ldots \longrightarrow c\, C + d\, D \ldots$$
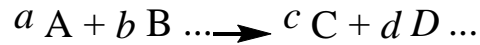
$$K = \frac{[C]^c [D]^d \ldots}{[A]^a [B]^b \ldots}$$

$$K = e^{\frac{-\Delta G}{RT}}$$

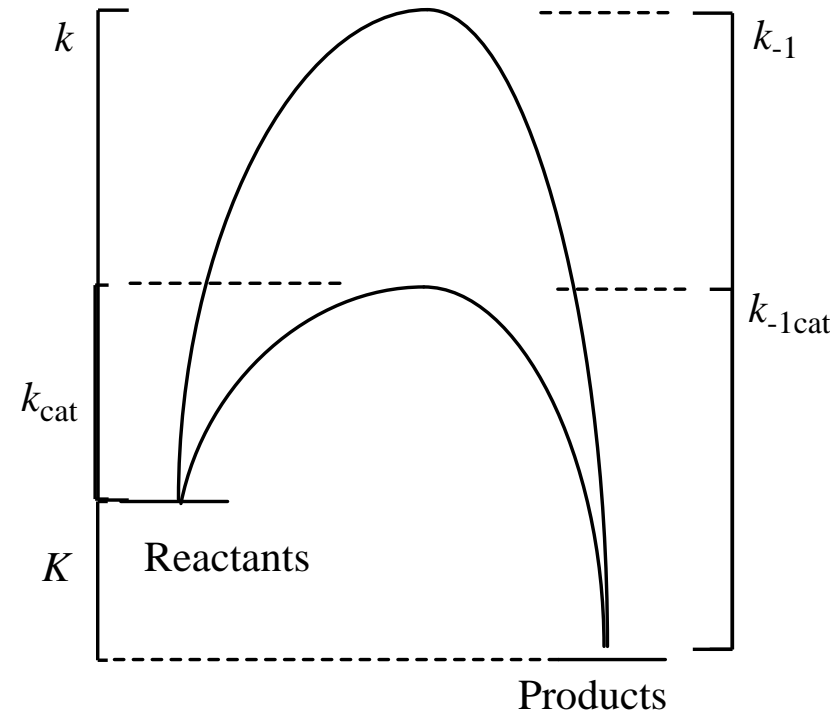- The activation barrier can be expressed as a rate constant.
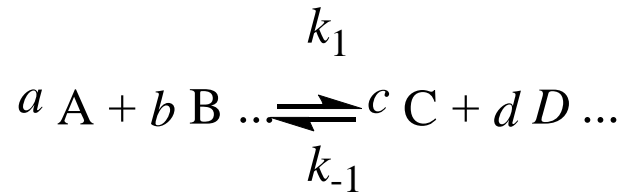
for an elementary (one step) reaction

$$a\, A + b\, B \ldots \longrightarrow c\, C + d\, D \ldots$$

$$\text{rate} = k[A]^a [B]^b \ldots$$

$$k = A e^{\frac{-\Delta G*}{RT}}$$

- A catalyst *cannot* make a reaction more favorable (no effect on K).
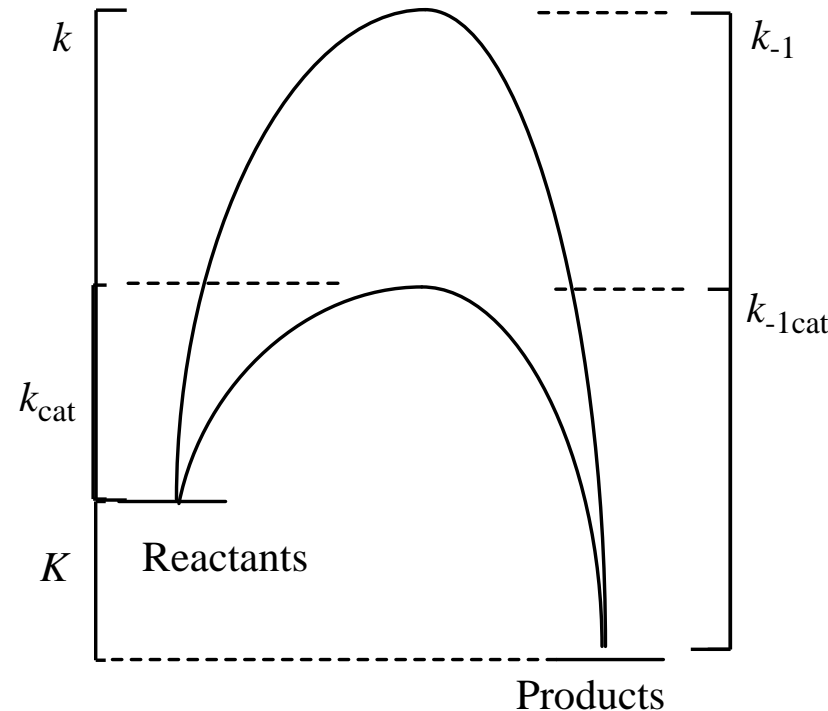
- A catalyst speeds the forward and reverse reaction rate.
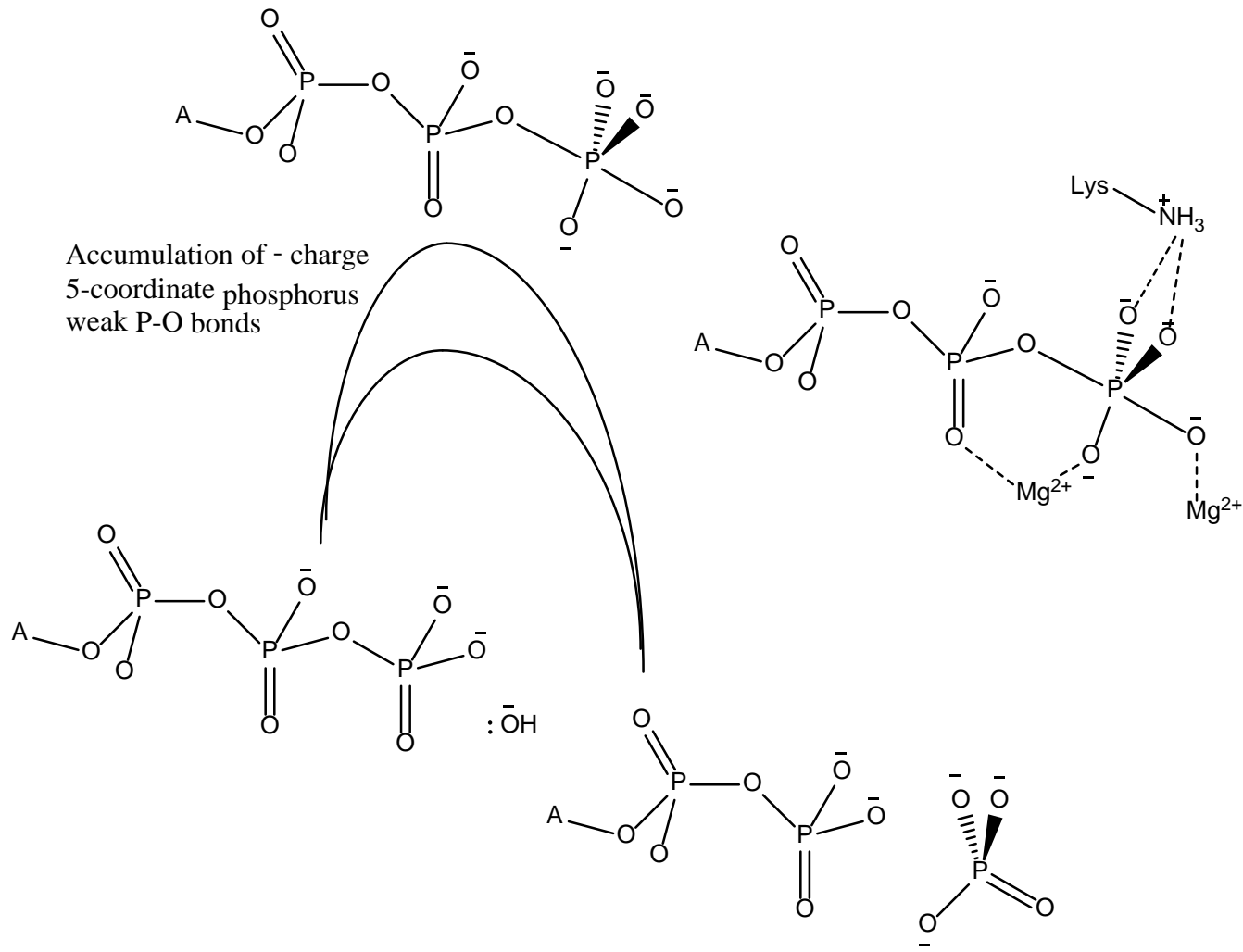
Relationship to equilibrium and rate constant.

$$a\,\text{A} + b\,\text{B} \ldots \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} c\,\text{C} + d\,\text{D} \ldots$$

$$\frac{k_1}{k_{-1}} = K$$

- If a catalyst lowers the forward rate constant, it lowers the reverse rate constant by the same amoung because K must stay the same.
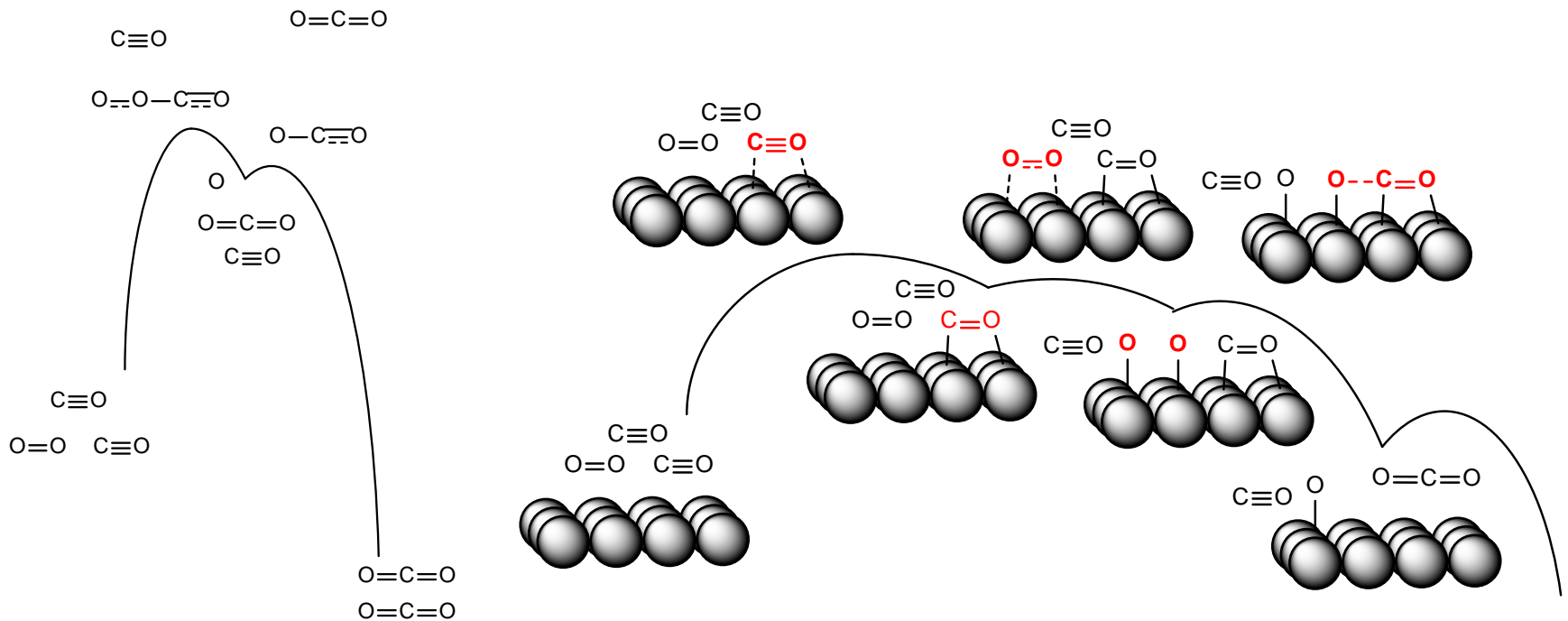
How do they work?

- Catalysts speed reactions by providing a pathway with low energy transition states
  - Can be the same transiton state, Ex: ATP hydrolysis

Accumulation of - charge
5-coordinate phosphorus
weak P-O bonds

: ŌH

How do they work?

- Catalysts speed reactions by providing a pathway with low energy transition states
  - Can be the different pathways altogether (burning CO vs. catalytic converter
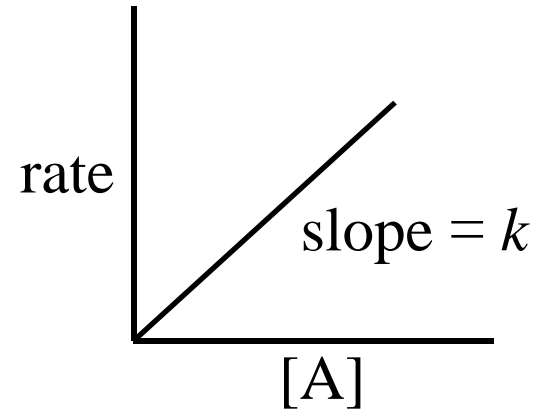
How do we figure out how they work?

- Mechanism – The set of specific elementary reactions that describe the transformation

- Kinetics-most important tool.

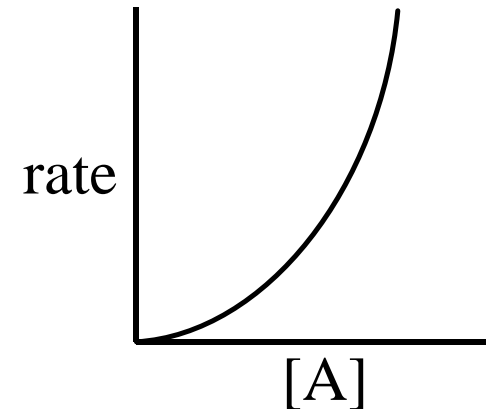- You can never prove a mechanism. You can only disprove mechanisms.

Kinetic behavior of simple reactions.

A $\longrightarrow$ B
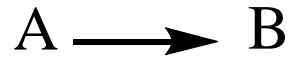
rate = $k_{[A]}$ 1st order reaction

rate

slope = k

[A]

2 A $\longrightarrow$ B

rate = $k_{[A]}^2$ 2st order reaction

rate

[A]

A + B $\longrightarrow$ C

rate = $k_{[A][B]}$ 2st order reaction,
1st order in A and in B

Bimolecular reaction: pseudo-first order kinetics

$$A + B \longrightarrow C$$

rate $= k_{[A][B]}$ 2st order reaction, 1st order in A and in B

- Hold one reagent in excess (10x), and that reagent changes negligibly.
  - Ex. 0.1 M A, and 0.01 M B. When B is consumed, [A] has barely changed (0.09 M). Thus, [A] is effectively constant.
  - [A] is constant, so k[A] is constant. We rename this k_ψ (k-pseudo)
  - Thus, we call these conditions "pseudo-first order'

$$k_{[A]} = k_\psi$$
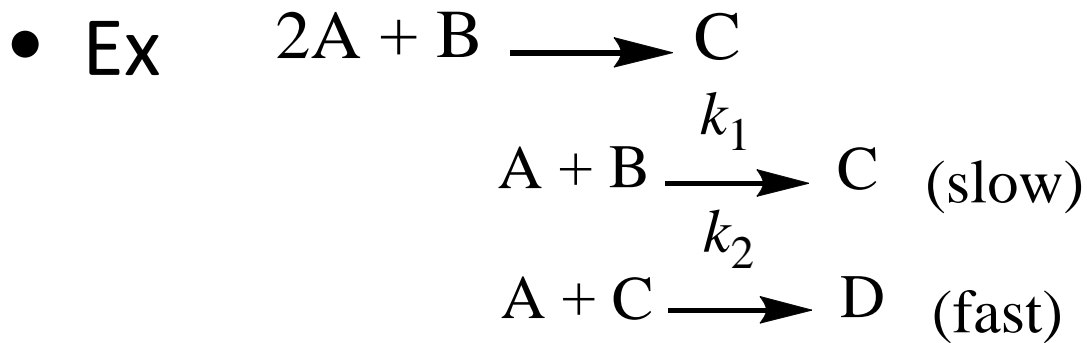$$\text{rate} = k_{[A][B]} = k_\psi[B]$$

Pseudo-first order kinetics

$$\text{rate} = k_{\psi}[B]$$

rate

slope $= k_{\psi} = k_{[A]}$

[B]
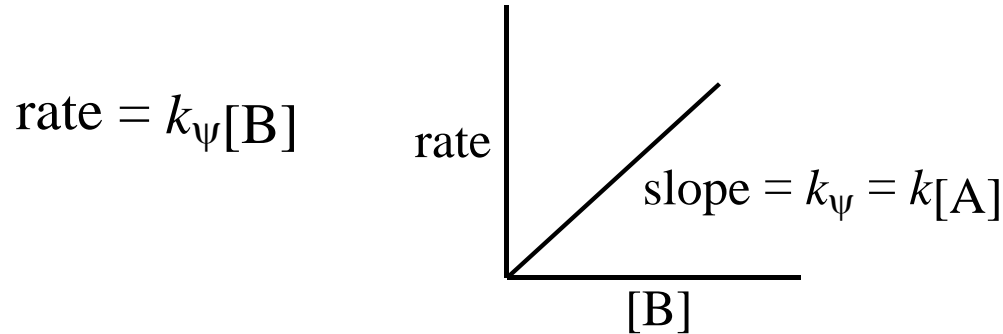
- Finally, divide k_{ψ} by known concentration of A to determine k.
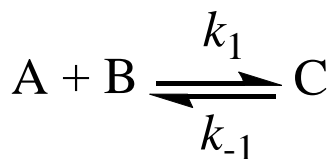
More complicated mechanisms.

- In a multi-step mechanism, only the slowest step matters (rate-determining step)
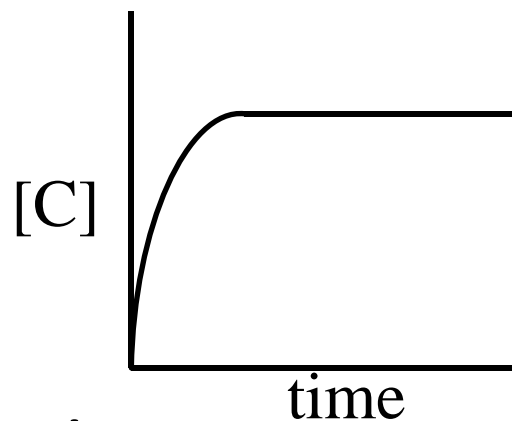
- Ex $2A + B \longrightarrow C$

$$A + B \xrightarrow[k_2]{k_1} C \quad \text{(slow)}$$

$$A + C \xrightarrow{k_2} D \quad \text{(fast)}$$

- Write rate law based upon slow step

- Rate = $k_1[A][B]$

Another example: steady-state approximation

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$C \xrightarrow{k_2} D \quad \text{(slow)}$$

$$\text{Rate} = k_2[C]$$

$$A + B \longrightarrow D$$

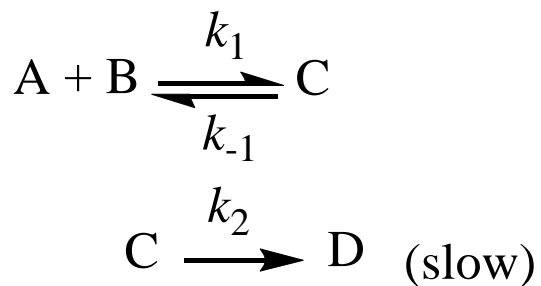[C] vs time graph

- Assume change in intermediate is zero

$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] - k_2[C] = 0$$

$$k_1[A][B] = k_{-1}[C] + k_2[C]$$

$$\frac{k_1}{(k_{-1}+k_2)}[A][B] = [C]$$
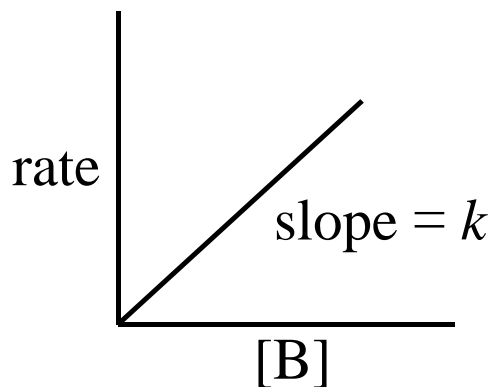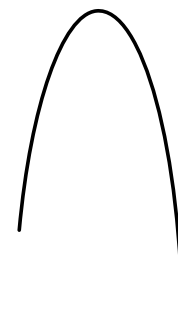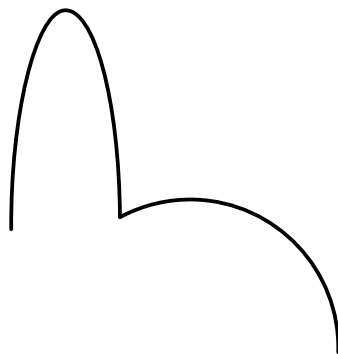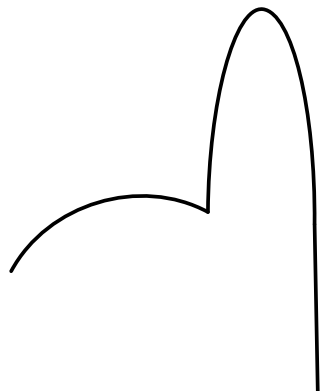
$$\text{Rate} = \frac{k_1 k_2}{(k_{-1}+k_2)}[A][B]$$

Reiterate: You can't prove a mechanism.

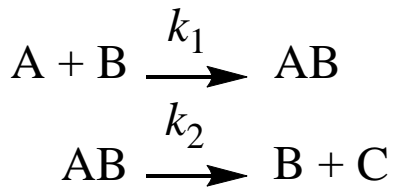$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$C \xrightarrow{k_2} D \quad \text{(slow)}$$

$$A + B \xrightarrow{k_1} C \quad \text{(slow)}$$

$$\xrightarrow{k_2}$$

$$A + C \longrightarrow D \quad \text{(fast)}$$
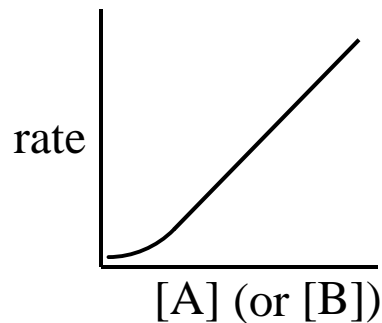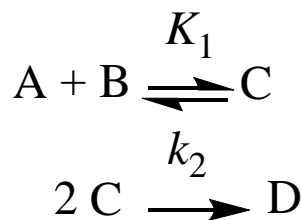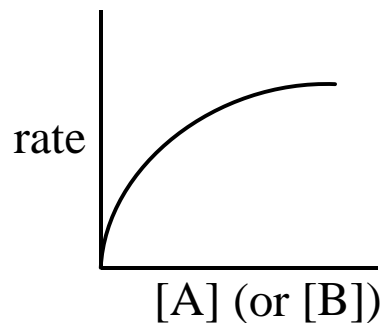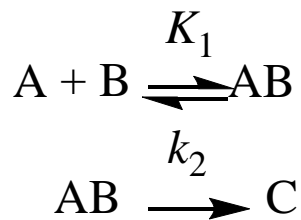
$$A + B \xrightarrow{k} D$$
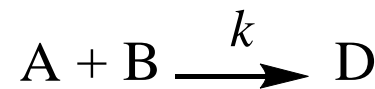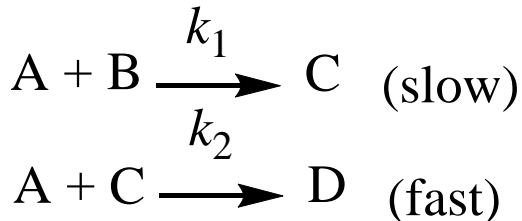
$$\text{Rate} = \frac{k_1 k_2}{(k_{-1} + k_2)} [A][B]$$

$$\text{Rate} = k_1[A][B]$$

$$\text{Rate} = k[A][B]$$

rate

slope = k

[B]

Other examples.

$$A + B \underset{k_2}{\overset{K_1}{\rightleftharpoons}} AB$$

$$AB \xrightarrow{k_2} C$$

rate vs [A] (or [B])

$$A + B \underset{k_2}{\overset{K_1}{\rightleftharpoons}} C$$

$$2\,C \xrightarrow{k_2} D$$

rate vs [A] (or [B])

$$A + B \xrightarrow{k_1} AB$$

$$AB \xrightarrow{k_2} B + C$$

(B is a catalyst)
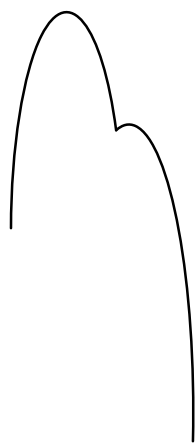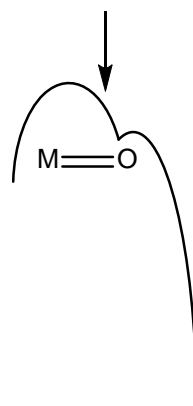

rate vs [A]

rate vs [B]
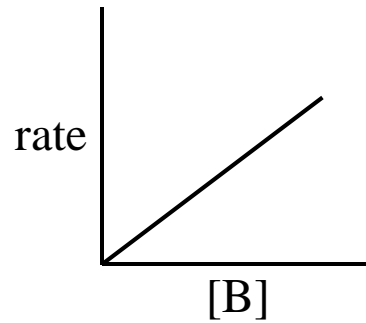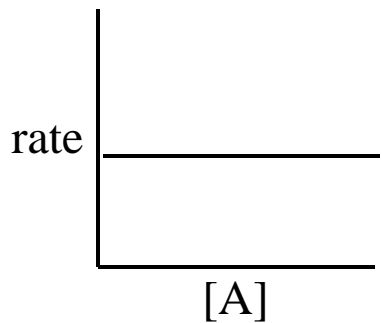
How do we design one?

- The goal is to lower the transition state.
- Often we make the mistake of trying to lower the energy of an intermediate instead.
- Ex, water oxidation: Plan

$$M + H_2O \longrightarrow M{-}OH + H^+$$

$$M{-}OH \longrightarrow M{=}O + 2\,e^-$$

$$2\,M{=}O \longrightarrow 2\,M + O_2$$

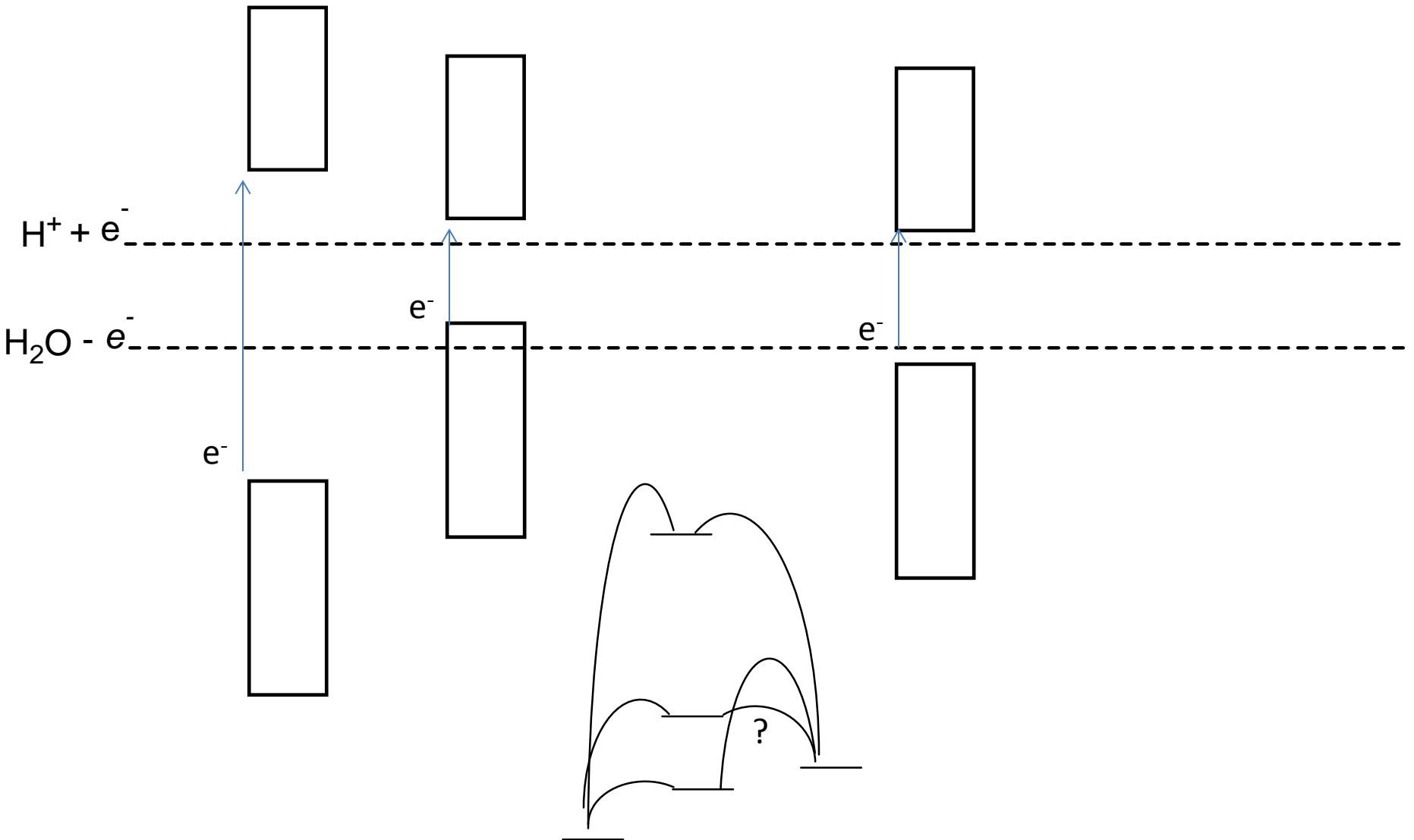lowered intermediate
and transition state

M═O

lowered intermediate
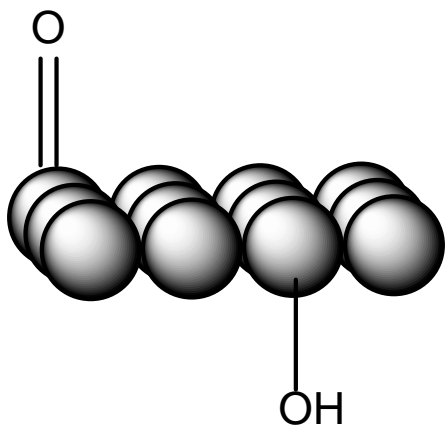and transition state

M═O

Redox catalysis.

- Band structure/orbital energy is important.

Also important is 3D constellation of intermediates